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PRELIMINARY DETERMINATION OF THE THERMAL EXPANSION OF MOLYBDENUM

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The work described in this paper was undertaken for the purpose of satisfying an increasing demand for accurate data on the thermal expansion of molybdenum.

PREPARATION OF SPECIMEN

The Pfanstiehl Co., of Chicago, kindly furnished the specimen which was carefully made in the research laboratory of that company, and, while not of the purity required for atomic weight determinations, it was purer than the ordinary commercial molybdenum. The specimen was made from the powdered material, which was put through a process similar to that used by the company in making tungsten rods for contact points. After being sintered it was heated to approximately 1050° C in a hydrogen atmosphere and swaged to the desired size.

CHEMICAL COMPOSITION AND DENSITY

The chemical composition [1] was found to be as follows: Molybdenum 99.85 per cent, iron 0.12 per cent, silicon 0.015 per cent, and sulphur 0.002 per cent. The density [2] after the thermal expansion tests was 10.114 g/cm^3 at 15° C.

APPARATUS

The determinations were made in the Bureau of Standards expansivity laboratory, which is devoted exclusively to the measurement of the expansion of solids, and is equipped with apparatus [3] designed for the double purpose of obtaining good temperature uniformity and high accuracy in measuring length changes.

For this investigation the specimen was supported in a return-flow bath filled with oil or pentane, the liquid used depending on the temperature desired. For temperatures between room and 300° C Renown engine oil was used, but for low temperatures pentane was employed. An electric resistance coil surrounded by and in contact with the liquid was used for heating. Cooling below room temperature was effected by the expansion of compressed air within a coil of copper tubing immersed in the bath containing pentane. The liquid surrounding the specimen was kept in circulation by means of a propeller. The temperature variation over the entire specimen was probably not greater than 0°1 during an observation.

The length changes were determined with a comparator consisting of two microscopes rigidly clamped on an invar bar at a distance from each other equal to the length of the specimen (20 cm). The microscopes were so arranged that they could be first sighted on a standard length bar kept at constant temperature and then on the 1-mil wires which were in contact with the ends of the specimen under test.[4]

The temperatures were determined by means of a copper-constantan thermoelement and a potentiometer calibrated, respectively, by the heat and electrical divisions of this Bureau.

RESULTS OF TEST 1

The results obtained in the first test are shown in the following tables and the accompanying curve (Fig. 1):

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[1] Determined by G. E. F. Lundell and J. A. Scherrer, of this Bureau.

[2] Determined by E. L. Peffer, of this Bureau.

[3] This apparatus will be described in detail in a Bureau publication.

[4] A. W. Gray, Journal of the Washington Academy of Sciences, 2, p. 248; 1912.

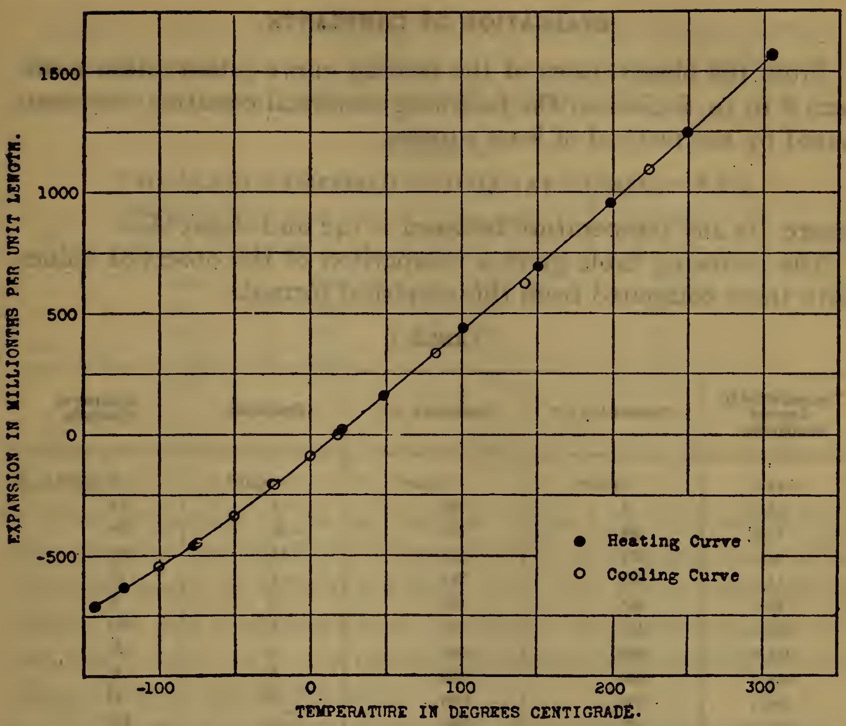

FIG. 1.—*Linear expansion of molybdenum as a function of temperature (Test 1, Table 1)*

Ordinates represent the change per unit length from the length at the initial temperature 17°8 C.

TABLE 1

Observation number	Date	Time	Temperature	ΔL*
	1917		°C	
1	Oct. 17	11.29 a. m.	17.8	0×10^{-6}
2	Oct. 17	12.34 p. m.	17.8	1.0
3	Oct. 17	12.47 p. m.	.2	− 88.7
4	Oct. 17	1.10 p. m.	− 23.5	−208.1
5	Oct. 17	....	− 50.0	−336.7
6	Oct. 17	2.11 p. m.	− 75.2	−450.6
7	Oct. 17	3.47 p. m.	− 99.8	−547.8
8	Oct. 17	4.03 p. m.	−142.5	−709.6
9	Oct. 17	4.20 p. m.	−123.1	−633.6
10	Oct. 17	4.40 p. m.	− 77.2	−460.9
11	Oct. 17	5.05 p. m.	− 24.4	−208.1
12	Oct. 18	9.36 a. m.	+ 18.7	+ 3.8
13	Oct. 18	10.04 a. m.	49.2	157.4
14	Oct. 18	10.45 a. m.	101.6	436.1
15	Oct. 18	11.20 a. m.	151.0	694.8
16	Oct. 18	11.52 a. m.	198.8	954.9
17	Oct. 18	12.32 p. m.	249.1	1247.2
18	Oct. 18	1.29 p. m.	305.2	1563.3
19	Oct. 18	1.49 p. m.	305.3	1569.9
20	Oct. 18	3.00 p. m.	223.9	1095.0
21	Oct. 18	3.30 p. m.	141.5	625.6
22	Oct. 18	3.55 p. m.	83.4	336.1
23	Oct. 19	9.28 a. m.	22.4	22.3

*ΔL represents the change per unit length from the length at the initial temperature 17°8 C.

EVALUATION OF CONSTANTS

From the observations of the heating curve (observation numbers 8 to 19, inclusive) the following empirical equation was computed by the method of least squares:

$$\triangle L^* = 4.090(t+142.5)10^{-6} + 0.00226(t+142.5)^2 10^{-6}$$

where t is any temperature between −142 and +305° C.

The following table gives a comparison of the observed values with those computed from this empirical formula:

TABLE 2

Temperature in degrees centigrade	Observed $\triangle L$*	Computed $\triangle L$	Residuals	Squares of residuals
−142.5	0×10^{-6}	0×10^{-6}	0×10^{-6}	0×10^{-12}
−123.1	76	80	− 4	16
− 77.2	249	277	−28	784
− 24.4	502	515	−13	169
+ 18.7	713	718	− 5	25
49.2	867	867	0	0
101.6	1146	1133	+13	169
151.0	1404	1395	9	81
198.6	1664	1658	6	36
249.1	1957	1948	9	81
305.2	2273	2284	−11	121
305.3	2280	2285	− 5	25
				1507×10^{-12}

The sum of the squares of the residuals is 1507×10^{-12} and hence $r=0.6745\sqrt{\frac{1507\times10^{-12}}{12-2}} = \pm 8.3\times10^{-6}$ per unit length is the probable error of a single computed value if the observations be regarded as exact, or the probable error of an observation if the law expressed in the empirical formula be regarded as exact.

From a consideration of the performance of the apparatus it is believed that the maximum error of observation does not exceed $\pm5\times10^{-6}$, and therefore the experimental probable error of a single observation is less than $\pm5\times10^{-6}$. The authors are therefore led to believe that a part of the probable error, $\pm8.3\times10^{-6}$, represents the amount by which the expansion fails to follow the quadratic law as expressed in the above equation.

The value obtained for the probable error is affected by the departure of the expansion curve from the parabolic law. That this departure exists is witnessed by the continuity of the signs of the residuals in Table 2.

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*$\triangle L$ represents the change per unit length from the length at the lowest temperature −142°5 C. The values of Table 2 are obtained by adding 709.6 to observations 8 to 19 of Table 1.

Table 3 shows the deviations of the observed values (observation numbers 19 to 23, inclusive) of the cooling curve from this empirical equation representing the heating curve.

TABLE 3

Temperature in degrees centigrade	Observed ΔL*	Computed ΔL	Deviations
305.3	2280×10^{-6}	2285×10^{-6}	-5×10^{-6}
223.9	1805	1802	+3
141.5	1335	1344	−9
83.4	1046	1039	+7
22.4	732	736	−4

The average deviation of the cooling curve from the computed heating curve is $\pm 5.6\times10^{-6}$.

From inspection of the residuals in Table 2, it is apparent that the previous second degree equation does not satisfy with sufficient accuracy all the observations over the whole temperature range. It was found necessary to obtain two equations, one for the range from −142° to room temperature and another for the range above room temperature.

The following equation, computed from observation numbers 1 to 12, inclusive,

$$\Delta L^* = 3.522(t+142.5)10^{-6} + 0.00570(t+142.5)^2 10^{-6}$$

satisfies the observations below room temperature. A comparison of all the observed values below room temperature with those computed from this equation is given in the following table:

TABLE 4

Temperature in degrees centigrade	Observed ΔL*	Computed ΔL	Residuals
17.8	710×10^{-6}	711×10^{-6}	-1×10^{-6}
17.8	711	711	0
0.2	621	619	+2
− 23.5	502	500	+2
− 50.0	373	375	−2
− 75.2	259	263	−4
− 99.8	162	161	+1
−142.5	0	0	0
−123.1	76	70	+6
− 77.2	249	254	−5
− 24.4	502	495	+7
+ 18.7	713	716	−3

* ΔL represents the change per unit length from the length at the temperature −142°5 C.

The probable error of a single observation is $\pm 2.6 \times 10^{-6}$.

From the observations of the heating curve (room temperature to $+305^\circ$ C), the following empirical equation was computed:

$$\Delta L^* = 5.088(t-18.7)10^{-6} + 0.00126(t-18.7)^2 10^{-6}$$

where t is any temperature between 19 and 305° C.

The following table gives a comparison of the observed values with those computed from this empirical formula:

TABLE 5

Temperature in degrees centigrade	Observed ΔL*	Computed ΔL	Residuals
18.7	0×10^{-6}	0×10^{-6}	0×10^{-6}
49.2	154	156	−2
101.6	432	430	+2
151.0	691	695	−4
198.6	951	956	−5
249.1	1243	1239	+4
305.2	1560	1561	−1
305.3	1566	1562	+4

The probable error of a single observation is $\pm 2.5 \times 10^{-6}$.

Table 6 shows the deviations of the observed values (observation numbers 19 to 23, inclusive) of the cooling curve from this empirical equation representing the heating curve.

TABLE 6

Temperature in degrees centigrade	Observed ΔL*	Computed ΔL	Deviations
305.3	1566×10^{-6}	1562×10^{-6}	$+4 \times 10^{-6}$
223.9	1091	1097	− 6
141.5	622	644	−22
83.4	332	334	− 2
22.4	18	19	− 1

The average deviation of the cooling curve from the computed heating curve is 7.0×10^{-6}. From these deviations it is apparent that the cooling curve lies slightly below the heating curve.

The two equations of expansion expressed in terms of L_0, the length of the material at 0° C, are

$$L_t = L_0(1 + 5.15t \times 10^{-6} + 0.00570t^2 \times 10^{-6}) \text{ and}$$
$$L_t = L_0(1 + 5.04t \times 10^{-6} + 0.00126t^2 \times 10^{-6})$$

where L_t is the length of the specimen at any temperature t within the proper range; in the first case 19 to -142° C and in the second case 19 to $+305^\circ$ C.

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* ΔL represents the change per unit length from the length at the temperature $18^\circ.7$ C.

RESULTS OF TEST 2

Several days later observations were taken from room temperature to 304° C. The results obtained on the second test of the same specimen are shown in Table 7 and Fig. 2.

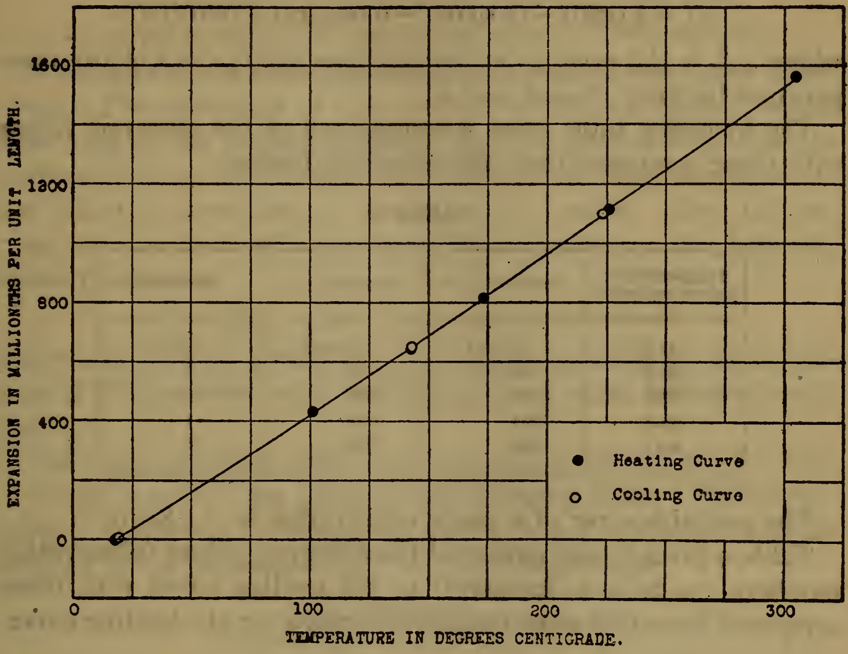

FIG. 2.—*Linear expansion of molybdenum as a function of temperature (Test 2, Table 7)*

TABLE 7

Observation number	Date	Time	Temperature	ΔL *
	1917		°C	
1-a	Oct. 22	10.19 a. m.	18.0	0×10^{-6}
2-a	Oct. 22	11.15 a. m.	101.3	430
3-a	Oct. 22	11.51 a. m.	173.2	816
4-a	Oct. 22	12.35 p. m.	225.8	1115
5-a	Oct. 22	1.42 p. m.	304.5	1565
6-a	Oct. 22	2.43 p. m.	223.2	1099
7-a	Oct. 22	3.35 p. m.	143.1	648
8-a	Oct. 22	3.53 p. m.	142.8	643
9-a	Oct. 23	10.48 a. m.	19.8	4

* ΔL represents the change per unit length from the length at the initial temperature 18° C.

EVALUATION OF CONSTANTS

From the observations (numbers 1–a to 5–a, inclusive) of the heating curve the following empirical equation was computed by the method of least squares:

$$\Delta L = 5.038(t-18.0)10^{-6} + 0.00149(t-18.0)^2 10^{-6}$$

where ΔL is the same as in the previous table, and t is any temperature between 18 and 304° C.

The following table gives a comparison of the observed values with those computed from this empirical formula:

TABLE 8

Temperature in degrees centigrade	Observed ΔL*	Computed ΔL	Residuals
18.0	0×10^{-6}	0×10^{-6}	0×10^{-6}
101.3	430	430	0
173.2	816	818	−2
225.8	1115	1111	+4
304.5	1565	1566	−1

The probable error of a single observation is $\pm 1.8 \times 10^{-6}$.

Table 9 gives a comparison of the observed values (observation numbers 5–a to 9–a, inclusive) of the cooling curve with those computed from this same empirical formula for the heating curve.

TABLE 9

Temperature in degrees centigrade	Observed ΔL*	Computed ΔL	Deviations
304.5	1565×10^{-6}	1566×10^{-6}	-1×10^{-6}
223.2	1099	1097	+2
143.1	648	654	−6
142.8	643	652	−9
19.8	4	9	−5

The average deviation of the cooling curve from the computed heating curve is 4.6×10^{-6} per unit length.

On the second heating the length at any temperature between 18 and 304° C may be represented by the following empirical equation:

$$L_t = L_o(1 + 4.98t \times 10^{-6} + 0.00149t^2 \times 10^{-6})$$

---

*ΔL represents the change per unit length from the length at the initial temperature 18° C.

COMPARISON OF TESTS

From the observations of the two tests two quadratic equations were obtained which satisfy the observations above room temperature. These equations are

$$L_t = L_0(1 + 5.04t \times 10^{-6} + 0.00126t^2 \times 10^{-6}). \quad \text{First test.}$$

$$L_t = L_0(1 + 4.98t \times 10^{-6} + 0.00149t^2 \times 10^{-6}). \quad \text{Second test.}$$

A comparison of these equations will show a very close agreement. The coefficient of t in the first equation is slightly larger than that in the second equation, but the reverse is true of the coefficient of t^2. The lengths determined from these equations do not differ by more than 4×10^{-6} per unit length. Since this approaches the limit of accuracy of the apparatus, the following average equation

$$L_t = L_0(1 + 5.01t \times 10^{-6} + 0.00138t^2 \times 10^{-6})$$

is given as the most probable second-degree equation for the expansion of this specimen of molybdenum from room temperature to 305° C.

The instantaneous coefficients computed for every 50° from −100 to +300° C are given in the following table. The instantaneous coefficient or rate of expansion at any temperature is the tangent to the expansion curve at that temperature.

TABLE 10

Temperature in degrees centigrade	Instantaneous coefficients
−100	4.0×10^{-6}
− 50	4.6
0	5.1
+ 50	5.1
100	5.3
150	5.4
200	5.6
250	5.7
300	5.8

The work is being continued to secure values over a greater temperature range.

SUMMARY

1. The thermal expansion of molybdenum has been determined between −142 and +305° C.

2. It is impossible to secure a second-degree equation which adequately represents the behavior of the material throughout this temperature range.

3. The most probable equation applicable between −142 and +19° C is

$$L_t = L_o(1 + 5.15t \times 10^{-6} + 0.00570t^2 \times 10^{-6})$$

4. The most probable equation applicable between 19 and +305° C is

$$L_t = L_o(1 + 5.01t \times 10^{-6} + 0.00138t^2 \times 10^{-6})$$

5. The instantaneous coefficient or rate of expansion increases with temperature.

We are greatly indebted to Roger W. Eisinger for his aid in the computations; also to Dr. W. H. Souder for his valuable suggestions.

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